

## Claims

We claim:

1. A swellable polymer gel composition for use with an aqueous solution, the swellable polymer gel composition comprising:

water;

a water soluble polymer;

5 a water soluble crosslinking system;

wherein the amounts of the polymer and the crosslinking system are effective to form a substantially uniformly reacted gel structure; and

10 a swelling agent in an amount calculated to maintain or increase the volume of the gel a predetermined percentage when the swelling agent contacts the aqueous solution.

2. The swellable polymer gel composition of claim 1 wherein the composition further comprises a strengthening agent in an amount sufficient to increase the gel strength.

3. The swellable polymer gel composition of claim 1 wherein the water soluble polymer is selected from a group consisting of homopolymers of acrylamide, copolymers of acrylamide and vinyl pyrrolidone, homopolymers of methacrylamide, copolymers of acrylamide and methacrylamide, copolymers of acrylamide and acrylic acid, 5 copolymers of methacrylamide and acrylic acid, terpolymers of pyrrolidone, acrylamide and sodium 2-acrylamido-2-methylpropane sulfonate, copolymers of acrylamide and sodium 2-acrylamido-2-methylpropane sulfonate, water soluble cellulose ether, and derivatives and mixtures thereof.

4. The swellable polymer gel composition of claim 1 wherein the crosslinking system comprises:

- a water soluble crosslinking agent; and
- a water soluble reducing agent.

5. The swellable polymer gel composition of claim 4 wherein the crosslinking agent comprises a compound of a polyvalent metal reactive with the reducing agent and wherein the valence state of at least a portion of the metal is capable of being placed by the reducing agent in a valence state reactive with the polymer.

6. The swellable polymer gel composition of claim 5 wherein the crosslinking agent is selected from the group consisting of ammonium chromate, ammonium dichromate, the alkali metal chromates and dichromates, and derivatives and mixtures thereof.

7. The swellable polymer gel composition of claim 4 wherein the reducing agent is selected from the group consisting of thiourea, hydroquinone, sodium sulfide, sodium hydrosulfite, sodium metabisulfite, potassium sulfite, sodium bisulfite, potassium metabisulfite, sodium sulfite, sodium thiosulfate, ammonium thiosulfate, 5 potassium thiosulfate, potassium metabisulfate, ferrous sulfate, ferrous chloride, p-hydrazinobenzoic acid, hydrazine phosphite, hydrazine dihydrochloride, thioacetamide, and derivatives and mixtures thereof.

8. The swellable polymer gel composition of claim 1 wherein the crosslinking system comprises:

- a water soluble crosslinking agent; and
- a water soluble chelating agent.

9. The swellable polymer gel composition of claim 8 wherein the crosslinking agent is a compound of a polyvalent metal reactive with the chelating agent to retard the onset and rate of gelation of the crosslinking agent with the polymer.

10. The swellable polymer gel composition of claim 9 wherein the crosslinking agent is selected from the group consisting of iron (III), aluminum (III), titanium (IV), tin (IV), chromium (III), zirconium (IV), the metal cations of the first transition metal series, and derivatives and mixtures thereof.

11. The swellable polymer gel composition of claim 8 wherein the chelating agent is taken from the group consisting of acetate, nitrilotriacetate, tartrate, lactates, citrate, tripolyphosphite, metaphosphite, gluconate, phosphate, and mixtures and derivatives thereof.

12. The swellable polymer gel composition of claim 1 wherein the water contains not more than 5% monovalent or divalent metal salts.

13. The swellable polymer gel composition of claim 2 wherein the strengthening agent is selected from the group consisting of diatomaceous earth, agar, arabic gums, clays and clay-like materials, silica flour, natural fibers, synthetic fibers, cotton seed hulls, ground nut shells, finely divided natural sands, finely divided plastic particles, barium carbonate, barium sulfate, amorphous silica, barite, and derivatives and mixtures thereof.

14. The swellable polymer gel composition of claim 1 wherein the swelling agent is selected from the group consisting of poly(ethylene oxide), poly(vinyl alcohol), poly(acrylic acid), poly(acrylamide), poly(acrylonitrile), poly(N-vinyl pyrrolidone), poly(2-hydroxyethylmethacrylate), poly(N-alkylacrylamide), poly(N,N-dialkylacrylamide), poly(mono-N-alkylitconates), poly(gamma-glutamic acid),  
5 poly(L-glutamic acid), gel blends of each of the foregoing, copolymers with corresponding monomers, and derivatives and mixtures thereof.

15. The swellable polymer gel composition of claim 14 wherein the swelling agent is crosslinked acrylamide potassium acrylate copolymer.

16. The swellable polymer gel composition of claim 14 wherein the swelling agent is crosslinked acrylamide sodium acrylate copolymer.

17. The swellable polymer gel composition of claim 1 wherein the swelling agent is selected from the group consisting of chitosan, pectin, gelatin, amylopectin, k-carrageenan, hyaluronic acid, sulphobetaine, cellulose ethers, starch and derivatives and mixtures thereof.

18. The swellable polymer gel composition of claim 1 wherein the swelling agent is at least partially enclosed in an encapsulation material and wherein the encapsulation material is characterized by the ability to delay the swelling process.

19. The swellable polymer gel composition of claim 18 wherein the encapsulation material comprises a synthetic polymer taken from the group consisting of glycolide, poly(acrylate)s, poly(alkyl  $\alpha$ -cyanoacrylate) and poly(acrylamide).

20. The swellable polymer gel composition of claim 18 wherein the encapsulation material comprises a natural polymer taken from the group consisting of starch derivatives, cellulose derivatives, polysaccharides, chitosan, gelatin and carrageenans.

21. The swellable polymer gel composition of claim 1 wherein the weight of the polymer is from about 0.0025 to about 5 percent of the weight of the composition.

22. The swellable polymer gel composition of claim 4 wherein the crosslinking agent is from about 0.05 to about 60 weight percent of the polymer.

23. The swellable polymer gel composition of claim 4 wherein the weight of the reducing agent is from about 0.1 to about 300 percent of the stoichiometric amount of the reducing agent required to reduce the crosslinking agent to a reactive polyvalent valence state.

24. The swellable polymer gel composition of claim 8 wherein the amount of the chelating agent is effective to delay the availability of at least a portion of the polyvalent metal crosslinking agent for crosslinking with the polymer.

25. The swellable polymer gel composition of claim 2 wherein the weight of the strengthening agent is from about 0.01 to about 25 percent of the weight of the composition.

26. The swellable polymer gel composition of claim 1 wherein the weight of the swelling agent is from about 0.05 to about 5 percent of the weight of the composition.

27. The swellable polymer gel composition of claim 1 wherein the weight of the water is from about 75 percent to about 99 percent of the weight of the composition.

28. The swellable polymer gel composition of claim 1 wherein the polymer comprises a mixture of polymers, the mixture comprising:

carboxymethylcellulose having from about a 0.65 to about a 0.95 degree of substitution; and

5 partially hydrolyzed polyacrylamide having a degree of hydrolysis ranging from about 10 to about 20 percent;

wherein the weight of each polymer in the mixture of polymers is from about 0.01 to about 0.35 percent of the weight of the composition; and

10 wherein the polymers in the mixture are combined in about a 50/50 ratio.

29. The swellable polymer gel composition of claim 1 wherein the polymer comprises a mixture of polymers, the mixture comprising:

carboxymethylcellulose having from about a 0.65 to about a 0.95 degree of substitution; and

5 partially hydrolyzed polyacrylamide having a degree of hydrolysis ranging from about 10 to about 20 percent;

wherein the weight of each polymer in the mixture of polymers is from about 0.08 to about 1 percent of the weight of the composition; and

10 wherein the polymers in the mixture of polymers are combined in a ratio of about 70 percent carboxymethylcellulose to about 30 percent partially hydrolyzed polyacrylamide.

30. The swellable polymer gel of claim 4 wherein the crosslinking agent of the crosslinking system is sodium dichromate and wherein the weight of the sodium dichromate is from about 0.2 to about 60 percent of the weight of the polymer.

31. The swellable polymer gel composition of claim 30 wherein the reducing agent of the crosslinking system is selected from the group consisting of sodium thiosulfate or ammonium thiosulfate and wherein the weight of the reducing agent is from about 150 to about 500 percent of the weight of the sodium dichromate.

32. The swellable polymer gel composition of claim 6 wherein the crosslinking agent is sodium dichromate.

33. The swellable polymer gel composition of claim 8 wherein the crosslinking agent of the crosslinking system is zirconium lactate and wherein the weight of the crosslinking agent is from about 0.75 to about 3 percent of the weight of the composition.

34. The swellable polymer gel composition of claim 2 wherein the strengthening agent is diatomaceous earth and wherein the weight of the strengthening agent is from about 0.01 to about 25 percent of the weight of the composition.

35. The swellable polymer gel composition of claim 1 wherein the swelling agent is crosslinked sodium salt of polyacrylate and wherein the weight of swelling agent is from about 0.3 to about 5.0 percent of the weight of the composition.



36. A swellable polymer gel composition for use with an aqueous solution, the swellable polymer gel composition comprising:

water in an amount comprising from about 75 percent to about 99 percent of the weight of the composition;

5 a water soluble polymer comprising a mixture of polymers, wherein the mixture comprises:

carboxymethylcellulose having from about a 0.65 degree of substitution to about a 0.95 degree of substitution; and

10 partially hydrolyzed polyacrylamide having a degree of hydrolysis ranging from about 10 to about 20 percent;

wherein the weight of each polymer in the mixture of polymers is from about 0.01 to about 0.35 percent of the weight of the composition; and

15 wherein the polymers in the mixture of polymers are combined in about a 50/50 ratio;

a water soluble crosslinking system, the crosslinking system comprising a water soluble crosslinking agent and a water soluble reducing agent;

20 wherein the crosslinking agent is sodium dichromate and wherein the weight of the sodium dichromate is from about 0.2 to about 60 percent of the weight of the polymer; and

25 wherein the reducing agent is sodium thiosulfate or ammonium thiosulfate and wherein the weight of the reducing agent is from about 150 to about 500 percent of the weight of the sodium dichromate;

a strengthening agent comprising a mixture of diatomaceous earth and barite, wherein the weight of the strengthening agent is from about 0.01 to about 25 percent of the weight of the composition; and  
a swelling agent selected from the group consisting of crosslinked sodium salt of polyacrylate, crosslinked acrylamide potassium acrylate copolymer and crosslinked acrylamide sodium acrylate copolymer, wherein the weight of swelling agent is from about 0.3 to about 5.0 percent of the weight of the composition.

37. A swellable polymer gel composition for use with an aqueous solution, the swellable polymer gel composition comprising:

water in an amount comprising from about 75 percent to about 99 percent of the weight of the composition;

5 a water soluble polymer comprising a mixture of polymers, wherein the mixture comprises:

carboxymethylcellulose having from about a 0.65 degree of substitution to about a 0.95 degree of substitution; and

10 partially hydrolyzed polyacrylamide with a degree of hydrolysis ranging from about 10 to about 20 percent;

wherein the weight of each polymer in the mixture of polymers is from about 0.01 to about 0.35 percent of the weight of the composition; and

15 wherein the polymers in the mixture of polymers are combined in about a 50/50 ratio;

a water soluble crosslinking system, the crosslinking system comprising a water soluble crosslinking agent and a chelating agent, wherein the crosslinking agent is zirconium lactate comprising from about 0.75 to about 3 percent of the weight of the composition;

20 a strengthening agent comprising a mixture diatomaceous earth and barite, wherein the weight of the strengthening agent is from about 0.01 to about 25 percent of the weight of the composition; and

25 a swelling agent selected from the group consisting of crosslinked sodium salt of polyacrylate, crosslinked acrylamide potassium acrylate copolymer and crosslinked acrylamide sodium acrylate copolymer, wherein the weight of swelling agent is from about 0.3 to about 5.0 percent of the weight of the composition.

38. A swellable polymer gel composition for use with an aqueous solution, the swellable polymer gel composition comprising:

water in an amount comprising from about 75 percent to about 99 percent of the weight of the composition;

5 a water soluble polymer comprising a mixture of polymers, wherein the mixture comprises:

carboxymethylcellulose having from about a 0.65 degree of substitution to about a 0.95 degree of substitution; and

10 partially hydrolyzed polyacrylamide having a degree of hydrolysis ranging from about 10 to about 20 percent;

wherein the weight of each polymer in the mixture of polymers is from about 0.08 to about 1 percent of the weight of the composition; and

15 wherein the polymers in the mixture of polymers are combined in a ratio of about 70 percent carboxymethylcellulose to about 30 percent partially hydrolyzed polyacrylamide;

a water soluble crosslinking system, the crosslinking system comprising a water soluble crosslinking agent and a water soluble reducing agent;

20 wherein the crosslinking agent is sodium dichromate and wherein the weight of the sodium dichromate is from about 0.2 to about 60 percent of the weight of the polymer; and

wherein the reducing agent is sodium thiosulfate or ammonium thiosulfate and wherein the weight of the reducing agent is

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from about 150 to about 500 percent of the weight of the sodium dichromate;

a strengthening agent comprising a mixture of diatomaceous earth and barite, wherein the weight of the strengthening agent is from about 0.01 to about 25 percent of the weight of the composition; and

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a swelling agent selected from the group consisting of crosslinked sodium salt of polyacrylate, crosslinked acrylamide potassium acrylate copolymer and crosslinked acrylamide sodium acrylate copolymer, wherein the weight of swelling agent is from about 0.3 to about 5.0 percent of the weight of the composition.

39. A swellable polymer gel composition for use with an aqueous solution, the swellable polymer gel composition comprising:

water in an amount comprising from about 75 percent to about 99 percent of the weight of the composition;

5 a water soluble polymer comprising a mixture of polymers, wherein the mixture comprises:

carboxymethylcellulose having from about a 0.65 to about a 0.95 degree of substitution; and

10 partially hydrolyzed polyacrylamide with a degree of hydrolysis ranging from about 10 to about 20 percent;

wherein the weight of each polymer in the mixture of polymers is from about 0.08 to about 1 percent of the weight of the composition; and

15 wherein the polymers in the mixture of polymers are combined in a ratio of about 70 percent carboxymethylcellulose to about 30 percent partially hydrolyzed polyacrylamide;

20 a water soluble crosslinking system, the crosslinking system comprising a water soluble crosslinking agent and a chelating agent, wherein the crosslinking agent is zirconium lactate comprising from about 0.75 to about 3 percent of the weight of the composition;

a strengthening agent comprising a mixture of diatomaceous earth and barite, wherein the weight of the strengthening agent is from about 0.01 to about 25 percent of the weight of the composition; and

25 a swelling agent selected from the group consisting of crosslinked sodium salt of polyacrylate, crosslinked acrylamide potassium acrylate copolymer and crosslinked acrylamide sodium acrylate copolymer,

wherein the weight of swelling agent is from about 0.3 to about 5.0 percent of the weight of the composition.

40. The swellable polymer gel composition wherein the crosslinking system is further characterized by the ability to inhibit the leaching of toxic substances into the environment.



41. A method for treating a subterranean formation, the method  
5 comprising the steps of:

introducing a swellable composition into the formation in the area requiring  
treatment, wherein the swellable composition comprises:

a water soluble polymer;

a water soluble crosslinking system;

10 wherein the amounts of the polymer and the crosslinking system are  
effective to form a substantially uniformly reacted gel  
structure; and

a swelling agent in an amount calculated to maintain or increase the  
volume of the gel a predetermined percentage when the  
15 swelling agent contacts the aqueous solution.

42. The method of claim 41 wherein the composition is mixed at the  
site of the formation immediately before introducing the composition into the formation.

43. The method of claim 41 wherein the subterranean formation  
comprises an oil and gas well and wherein the treatment comprises plugging an oil or gas  
well to be abandoned.

44. The method of claim 43 wherein the oil and gas well defines a  
wellbore and wherein the method further comprises the steps of:

before introducing the swellable composition into the wellbore, circulating  
a fluid through the wellbore to remove existing fluids;

5 after introducing the swellable composition into the wellbore, removing  
equipment and tools from the wellbore; and

closing the wellbore to permit gelation and swelling of the composition.

45. The method of claim 44 wherein the step of circulating the fluid through the wellbore is accomplished by using the composition as the circulating fluid.

46. The method of claim 43 wherein the method further comprises the step of:

after abandoning the wellbore, restoring the well to service by circulating the composition out of the wellbore with a fluid.

47. A method for removably plugging an oil or gas well to be abandoned, wherein the well defines a wellbore and wherein the method comprises the step of plugging the wellbore with a composition, the composition being removable from the wellbore by circulating fluid through the wellbore.

48. A method for restoring to service an abandoned oil or gas well plugged with a composition removable from the wellbore, the method comprising the step of removing the composition from the wellbore by circulating a fluid through the wellbore.

49. The method of claim 41 wherein the subterranean formation comprises a producing oil or gas well and wherein the treatment comprises plugging and abandoning an oil or gas zone in the well.

50. The method of claim 49 wherein the oil or gas well defines a wellbore and wherein the method further comprises the steps of:

before introducing the swellable composition into the wellbore, localizing the zone to be plugged;

5 introducing the swellable composition into the wellbore to a predetermined depth above and below the localized zone;

sealing the swellable composition in the wellbore adjacent the localized zone; and

permitting gelation and swelling of the composition.

51. The method of claim 41 wherein the subterranean formation comprises an oil or gas well, the well defining a wellbore and wellbore casing, and wherein the treatment comprises sealing a leak in wellbore casing.

52. The method of claim 51 wherein the method further comprises the steps of:

before introducing the swellable composition into the wellbore, isolating the leak;

5 introducing the swellable composition into the environment in the area of the leak;

removing the swellable composition from wellbore;

permitting gelation and swelling of the composition in the area of the leak; and

10 restoring the well to service.

53. The method of claim 41 wherein the subterranean formation comprises an oil or gas well having failed a mechanical integrity test and wherein the treatment comprises repairing the oil or gas well.

54. The method of claim 53 wherein the well defines a wellbore and comprises production casing and tubing and wherein the method further comprises the steps of:

5 introducing the swellable composition into the annular space between the casing and the tubing;  
forcing the swellable composition through the leak in the casing;  
permitting gelation and swelling of the composition.

55. The method of claim 41 wherein the subterranean formation comprises an oil or gas well having a water bearing zone and wherein the treatment comprises reducing the amount of water produced from water bearing zone of the well.

56. The method of claim 55 wherein oil or gas well defines a wellbore and wherein the method further comprises the steps of:

5 introducing the swellable composition into the water producing zone;  
removing the swellable composition from the wellbore;  
5 allowing gelation and swelling of the composition in the water bearing zone; and  
restoring the well to service.